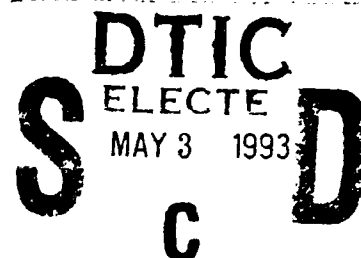


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by

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Dioxygen reduction in various acid electrolytes*

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(Received 2 November 1992)

Dioxygen reduction has been examined in several new acid electrolytes and mixtures of these electrolytes with concentrated phosphoric acid (used in present acid H₂O₂ fuel cells). The polarization curves have been determined on smooth platinum with the rotating disk and ring-disk electrodes and on high-area platinum with gas fed electrodes of the semi-hydrophobic type. The polarization is less than with concentrated H₃PO₄ in some of these alternative electrolytes. Possible explanations are discussed.

1. INTRODUCTION

The performance of the phosphoric acid fuel cell is limited principally by the irreversibility of the O₂ reduction reaction and the severe voltage losses at the air cathode. This irreversibility is in part caused by the strong adsorption of the electrolyte (particularly H₂PO₄⁻) on platinum catalyst. This has prompted the examination of alternative electrolytes to concentrated H₃PO₄.

O₂ reduction has been examined by the authors in a number of purified acid electrolytes including perfluorosulfonic, phosphoric, sulfonimide and carboxylic. These have been synthesized by Prof. D. Des Marteau of Clemson University and Prof. D. Burton of the University of Iowa. The polarization for O₂ reduction on smooth Pt as well as highly dispersed Pt of gas-fed O₂ cathodes is substantially lower in some of these electrolytes as well as their mixtures compared to concentrated H₃PO₄.

Several factors may be responsible for these differences in the polarization curves for O₂ reduction on smooth platinum as well as highly dispersed platinum. These include the following:

- differences in acidity
- specific ionic adsorption of the electrolyte
- differences in the compact layer structure at the interface
- differences in the solubility of O₂
- differences in the diffusion coefficient of O₂
- impurity effects.

* This paper is dedicated to Professor Aleksandar Despic on the occasion of his 65th birthday.

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These factors will be considered later in this paper in the discussion of the polarization data in these various acid electrolytes. In addition large changes in the conductivity may result in changes in the apparent polarization curves because of the difficulties in taking into account ohmic losses in the porous active catalyst layer. Differences in the wetting properties of the electrolyte can also have a major effect on the accessibility of the electrolyte to the electrocatalysts (e.g., Pt) in this active layer and produce major adverse effects on the voltage-current curves.

O₂ the various strong acids, CF₃SO₃H · H₂O would normally be among the most attractive in terms of low overpotential, lack of specific adsorption on Pt, high O₂ solubility and the know-how to clean this acid up with respect to adsorbable impurities.

Unfortunately the perfluorosulfonic acids have much lower ionic conductivity than H₃PO₄ at high concentrations and this leads to excessive ohmic loss that may more than offset the lower polarization at the air cathodes in fuel cells using this electrolyte. A further complication is that CF₃SO₃H at high concentration (6 M) wets Teflon and this causes flooding of the Teflon bonded gas diffusion electrodes.

II. MIXTURES OF CONCENTRATED PHOSPHORIC AND TRIFLUOROMETHANE-SULFONIC ACIDS

An alternative approach is the use of a mixture of H₃PO₄ with a strong acid such as CF₃SO₃H with both acids at high concentrations; e.g., 25 mol% of each acid and 50 mol% H₂O. The adsorption of the phosphate anion on the Pt surface can still occur but the activity of the phosphoric acid should be significantly depressed and this should reduce the adsorption of the phosphate anion on the Pt surface. The solubility of O₂ would still be increased although not by as much as with the pure CF₃SO₃H. The presence of the H₃PO₄ is expected to keep the conductivity of the electrolyte still quite high because of the Grotthus type conduction mechanism.

Prior work using laser Raman spectroscopy¹ has demonstrated that in the CF₃SO₃H · H₃PO₄ · H₂O system, the sulfonic acid is almost fully ionized and protonates both H₂O and H₃PO₄ for mole fractions of the sulfonic acid less than 0.4. Furthermore, these spectroscopic studies indicate that the formation of either the proton monohydrate (H₃O⁺) or the phosphonium ion [P(OH)₄⁺] is sufficient to promote the ionization of the CF₃SO₃H; i.e.,

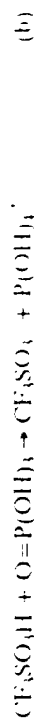
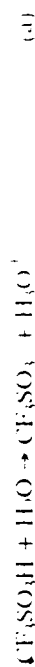


Figure 1 indicates the Tafel plots for O₂ reduction on smooth polycrystalline Pt in the CF₃SO₃H · H₃PO₄ · H₂O mixtures and in 86% H₃PO₄ at 25 °C. The measurements were made with the rotating disk technique; details are given elsewhere.² The abscissa corresponds to the current density *i* corrected for mass transport by multiplication by the factor *i*₀(*i*₀ - *i*) where *i*₀ is the diffusion limiting current density. For Fig. 1, the rotation rate was 1600 rpm. The Tafel slope in the potential region 0.7 to 0.7 V was ≈ 0.12 V/decade which at 25 °C corresponds to 2kT/e. The bending of the Tafel plot at more positive potentials is due to the initial stages of the anodic film

raises questions concerning the significance of the Tafel slopes for multistep electrode reactions involving adsorbed intermediates.

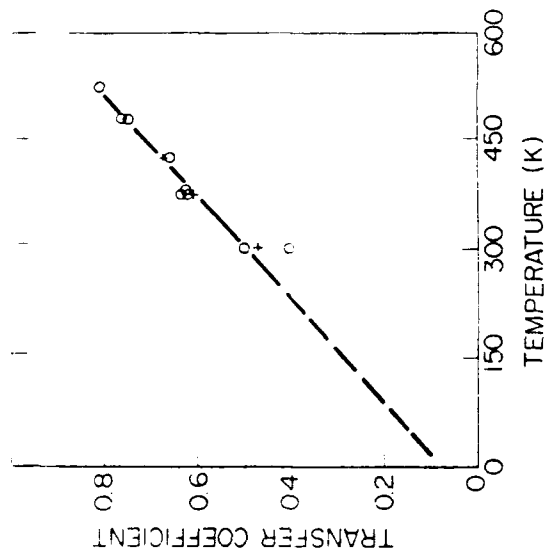


Fig. 2. Temperature dependence of apparent transfer coefficient for O_2 reduction in concentrated H_3PO_4 . (O) Clouser¹; (+) Huang *et al.*⁴

The first order rate constant is defined by the rate equation written in the form

$$i = 4FkP_{O_2} \cdot (i_d - i)/(i_d) \quad (1)$$

where P_{O_2} is the partial pressure (atm) of O_2 gas in equilibrium with the electrolytic solution. In Table I are listed the ratios of the rate constants (k_2) for the mixed acids to that (k_1) of the 86% H_3PO_4 , both at 0.80 V vs. RHE. The ratios of the rate constants were calculated using the following equation:

$$\frac{k_2}{k_1} = \left(\frac{(i_d)_1 - i}{i(i_d)_1} \right) \cdot \left(\frac{i_2(i_d)_2}{(i_d)_2 - i} \right) \quad (2)$$

with the condition that P_{O_2} and the potential are the same for both electrolytes. In Eq. (2), the subscripts 1 and 2 correspond to the measurement in H_3PO_4 and the mixed electrolytes, respectively.

The exchange current densities varied from 1.7×10^{-8} A/cm² for 86% H_3PO_4 to 7.5×10^{-8} A/cm² for the mixture with the highest TFMSA concentration, 25 mol% H_3PO_4 - 25 mol% TFMSA - 50 mol% H_2O at 25°C. The corresponding change in the ratio of the rate constants is $k_2/k_1 = 5.9$ at $E = 0.80$ V vs. RHE (see Table I). In this comparison, the number of electrons per O_2 molecule has been taken to be 4.0 and to be the same for all of the measurements corresponding to the linear region in the Tafel plots.

(PtOH) formation on Pt. The deviations from linearity in the Tafel plots at low potential may be due to a slight error in the i_d values used in constructing this figure. These were obtained from the slopes of the Koutecky - Levich plots of $1/i$ vs. $1/\omega^{1/2}$. As i approaches i_d , any error in i_d is greatly magnified. Another possibility is a kinetic limiting current associated with a step which is potential independent or which has only a very small potential dependence; e.g., the dissociative desorption of O_2 .

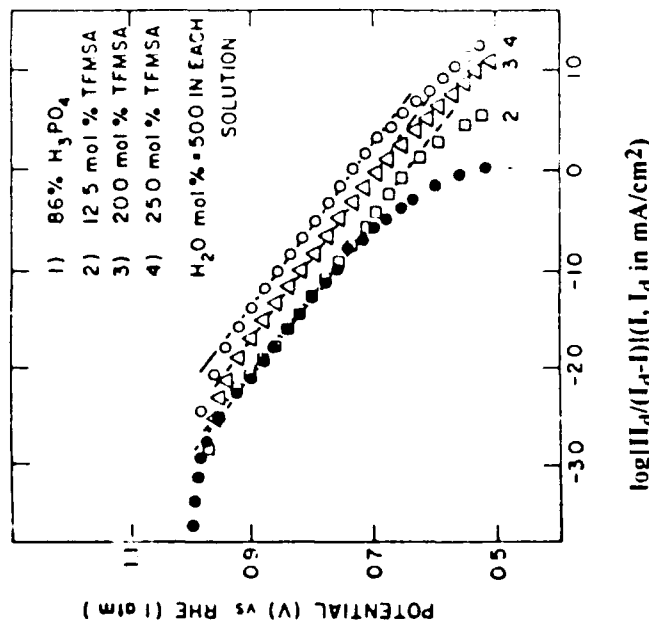


Fig. 1. Tafel plot for O_2 reduction in $CF_3SO_3H-H_3PO_4-H_2O$ mixture and in 86% H_3PO_4 at 25°C. i_d values (mA/cm²) are: (1) 0.116; (2) 0.728; (3) 1.35; (4) 2.08. Rotation rate = 1600 rpm.²

The reaction order with respect to O_2 has been confirmed as first order from the slope of plots of $\log i$ vs. $\log [(i_d - i)/i_d]$ obtained with the rotating disk electrode.² For example, for the 30 mol% H_3PO_4 - 20 mol% TFMSA - 50% H_2O solution, the slopes of these linear plots varied from 1.06 at 0.70 V to 1.10 at 0.55 V. No change in Tafel slope was obtained in going from 86% H_3PO_4 to 25% mol% TFMSA - 25% H_3PO_4 - 50% H_2O at 25°C.

Measurements in the authors' laboratory, however, indicate that the Tafel slope on bright polycrystalline Pt in the double layer region is almost independent of temperature over the range 25 to 250°C in concentrated H_3PO_4 and hence the apparent transfer coefficient is approximately proportional to the absolute temperature over this range (see Fig. 2).

The Tafel slope of -0.12 V/decade would ordinarily be taken as evidence that the rate determining step for O_2 reduction on Pt is the first electron transfer step. This

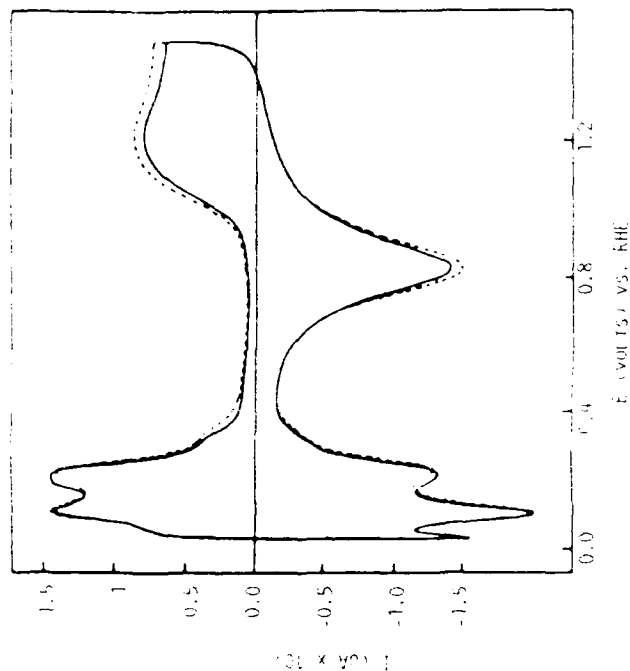


Fig. 3. Voltammograms of Pt in 85% H_3PO_4 (—) and 85% H_3PO_4 containing 4% PFSl (---) solutions saturated with N_2 ; sweep rate = 100 mV s^{-1} ; electrode area = 0.126 cm^2 ; $T = 20^\circ\text{C}$.

without O_2 present. This voltammogram plus others for more dilute solutions of PFSl in H_3PO_4 provide evidence that the PFSl is not strongly adsorbed on Pt while H_2PO_4^- is strongly adsorbed. Figure 4 presents the polarization curve recorded with the rotating disk electrode technique. The polarization curves for the 85% H_3PO_4 with and without 4% PFSl (Fig. 4) indicate that PFSl lowers the half wave potential $E_{1/2}$ by $\approx 90 \text{ mV}$ while the limiting current is increased by $\approx 64\%$.

TABLE II. Oxygen reduction at high surface area electrodes in sulfonyl acids and bisphosphonic acid solutions

Electrolyte	Temperature [$^\circ\text{C}$]	$E_{1/2}$ vs. H_2PO_4^- [mV]	i
84% $(\text{FSO}_2)_2\text{NH}$	70	-35	-105
84% $(\text{CF}_3\text{SO}_2)_2\text{NH}$	70	50	35
85% $\text{PO}(\text{OH})_2\text{CF}_2\text{CF}_2$	100	-100	70
85% H_3PO_4 plus less than 0.1% $(\text{CF}_3\text{SO}_2)_2\text{CH}_2\text{SO}_2\text{CF}_2\text{CF}_2$	100	45	30
85% H_3PO_4 plus 0.5% $\text{CF}_3\text{SO}_2\text{NHISO}_2\text{CF}_2\text{CF}_2$	70	70	70

The mixture of 85% H_3PO_4 and 4% PFSl has the milky appearance of an emulsion. At high concentrations H_3PO_4 solutions involves a three-dimensional strongly hydrogen bonded structure and the PFSl tends to be squeezed out of the bulk

TABLE I. Comparison of kinetic parameters for O_2 reduction in $\text{CF}_3\text{SO}_2\text{H}-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$ mixture at 25°C

Electrolyte $\text{H}_3\text{PO}_4-\text{CF}_3\text{SO}_2\text{H}-\text{H}_2\text{O}$ (mol%)	i_d (mA/cm^2)	$\frac{i_d}{B}$ (mA/cm^2) ^{1/2}	$i_d/(i_d - i)$ (mA/cm^2) ^{1/2}	k_2/k_1 (at 0.80 V)
50	0	50	2.9×10^{-3}	5.3×10^{-2}
37.5	12.5	50	1.82×10^{-2}	5.38×10^{-2}
30.0	20.0	50	3.38×10^{-2}	1.51×10^{-2}
25.0	25.0	50	5.2×10^{-2}	31.4×10^{-2}

k_1 = rate constant for 50 mol % H_3PO_4 -50 mol % H_2O ($\approx 86\%$ H_3PO_4)

k_2 = rate constant for mixed acids

$B = 0.62 n F D^{1/2} v^{1/2} C_{\text{O}_2}$, obtained from Koutecky-Levich plots

i_d = diffusion limiting current density

The k_2/k_1 ratios are close to unity for the acid mixtures with up to 12.5 mol% TFMSA but deviate substantially from unity for higher mol% of TFMSA (see Table I). Several factors can contribute to the change of the k_2/k_1 ratio including changes in the activity coefficient in the transition state, the activities of H_2O and the partially solvated protons and the adsorption of phosphate species on the Pt surface. Impurity effects cannot be discarded as a possible factor contributing to the change of the k_2/k_1 ratio at high H_3PO_4 and TFMSA concentration since these acids are difficult to purify to the extent that the Pt surface is completely free of impurities. The faster kinetics in the concentrated $\text{CF}_3\text{SO}_3\text{H}$ solution in Table I and Fig. 1 may be caused by a decrease in the adsorption of the H_2PO_4^- on the Pt surface and/or the higher solubility of O_2 in the concentrated $\text{CF}_3\text{SO}_3\text{H}$ compared with 86% H_3PO_4 .

The results on smooth Pt suggest that the addition of a strong acid to concentrated H_3PO_4 will lower the polarization for O_2 reduction at high performance gas-fed O_2 cathodes using highly dispersed Pt as the catalyst in phosphoric acid fuel cells. TFMSA, however, is not attractive as an additive in fuel cells operating at temperatures of $\approx 190^\circ\text{C}$ because of its volatility. The addition of TFMSA to concentrated H_3PO_4 also decreases the conductivity. In concentrated H_3PO_4 , extensive hydrogen bonding occurs and the conduction is principally by a Grotthus-type conduction mechanism involving protons hopping between adjacent H_3PO_4 molecules. The TFMSA reduces the intermolecular hydrogen bonding and thus reduces the conductivity. The increased ohmic loss is likely to offset much of the gain in cell voltage associated with the decrease in polarization of the O_2 cathode.

III. O_2 REDUCTION WITH PERFLUORINATED SULFONIMIDE AS AN ADDITIVE TO CONCENTRATED H_3PO_4

Some of the perfluorinated phosphoric, phosphonic, sulfonic, sulfonimide and carboxylic electrolytes have substantial effects on the O_2 electrode polarization even when added at relatively low concentrations to 85% H_3PO_4 ^{6,7} (see Table II).

Of particular interest are the perfluorosulfonimides (PFSl), such as the strong acid $\text{CF}_3\text{SO}_2\text{N}(\text{H})\text{SO}_2\text{CF}_3$. The voltammetry curves for Pt in N_2 saturated 85% H_3PO_4 with and without 4% (0.16 M) of this PFSl are shown in Fig. 3. The addition of the PFSl has relatively little effect on the voltammetry curve for Pt in 85% H_3PO_4

H₃PO₄ solution forming a physically adsorbed layer at the electrode surface with the hydrocarbon C₄F₉ tail probably oriented towards the electrode surface and the polar end towards the bulk solution. The structure of this layer including its thickness needs to be established. *In-situ* spectroscopic techniques such as infrared reflectance (SNIF-TIRS, EMIRS) and Raman (SERS) should be able to provide such information.

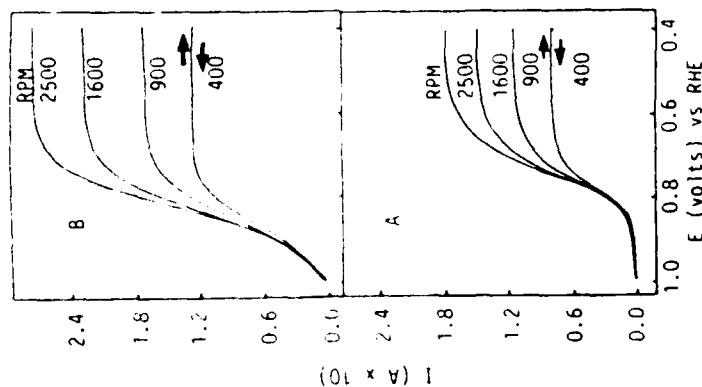


Fig. 4 (A) Polarization curves⁷ for O₂ reduction on a Pt rotating disk electrode (area = 0.126 cm²) in 85% H₃PO₄ solution saturated with O₂ at 1 atm; sweep rate = 10 mV s⁻¹; T = 20 °C. (B) Solution 85% H₃PO₄ + 4% PFSL. Other conditions same as for Fig. 4a.

The physically adsorbed PFSL layer at the electrode surface perturbs the structure of the double layer and lowers the effective dielectric constant adjacent to the electrode surface. The chemical potentials of adsorbed ionic species as well as H₃PO₄ and water molecules are dependent on the dielectric properties in the electrolyte phase immediately adjacent the Pt electrode. The O₂ molecule is relatively non-polar and the decrease in dielectric constant is expected to favor O₂ adsorption, not so much because of a direct interaction with the (O₂)_{ads} but rather through the destabilization of adsorbed more polar species and the freeing up of more adsorption sites for O₂. The PFSL layer is probably only a single molecule thick and does not seem to interfere with O₂ and water/proton transport at this interface. This layer resembles a self-ordered Langmuir-Blodgett film with the fluorocarbon end towards the platinum. In this layer O₂ has a higher concentration than in the bulk H₃PO₄ and H₂O has a lower concentration⁷ than in the bulk solution.

The PFSL is a relatively strong acid ($pK_a = 0.91$) compared with the first ionization of H₃PO₄ ($pK_{a1} = 2.15$). The solubility of the PFSL in 85% H₃PO₄, however, is slightly less than 0.5% and the PFSL in excess of 0.5% forms an emulsion. The addition of 4% PFSL would suppress the ionization of the H₃PO₄ but the hydrogen ion concentration would change by only a small amount (less than 1%).

The generation of H₂O₂ was monitored with the rotating ring-disk technique with a potential of 1.1 V vs. RHE applied to the ring while scanning the disk potential from 1.0 to 0.40 V. The ratio of the peroxide oxidation current on the ring electrode to the O₂ reduction current on the disk was very small and essentially the same with and without the 4% PFSL. In Fig. 4 the increase in the diffusion limiting current density in the rotating disk experiment with 4% PFSL added to 85% H₃PO₄ is relatively large (64% at 2500 rpm) and depends on the change in O₂ solubility and diffusion coefficients of the O₂ in the electrolytic solution. These were determined using the microelectrode technique.⁸ The solubility and diffusion coefficients are given in Table III. Both O₂ solubility and diffusion coefficients are much larger in the 84% PFSL than the 85% H₃PO₄. The difference in the $CD^{2/3}$ product for the 85% H₃PO₄ and 84% PFSL is sufficient to account for the 64% increase in limiting current density with 4% PFSL added to 85% H₃PO₄.

TABLE III The solubility and diffusivity of O₂ determined using a Pt micro disk electrode at 20 °C in various electrolytes

Electrolytes	Solubility (mol l ⁻¹)	Diffusion coefficient (cm ² s ⁻¹)
85% H ₃ PO ₄	$3.3 \pm 0.4 \times 10^{-4}$	$1.27 \pm 0.5 \times 10^{-6}$
80% C ₂ F ₅ PO(OH) ₂	$3.7 \pm 0.2 \times 10^{-3}$	$1.44 \pm 0.2 \times 10^{-6}$
75% C ₂ F ₅ PO(OH) ₂	$6.0 \pm 0.3 \times 10^{-3}$	$1.6 \pm 0.3 \times 10^{-6}$
84% (C ₂ F ₅ SO ₂) ₂ NH	$3.8 \pm 0.2 \times 10^{-3}$	$6.53 \pm 0.3 \times 10^{-6}$
92% (C ₂ F ₅ SO ₂) ₂ NH	$1.6 \pm 0.1 \times 10^{-2}$	$4.40 \pm 0.1 \times 10^{-6}$
84% C ₂ F ₅ SO ₂ NH(SO ₂) ₂ C ₂ F ₅	$4.7 \pm 0.2 \times 10^{-3}$	$5.97 \pm 0.2 \times 10^{-6}$
85% C ₂ F ₅ SO ₂ NH(SO ₂) ₂ C ₂ F ₅	$5.4 \pm 0.2 \times 10^{-3}$	$6.87 \pm 0.1 \times 10^{-6}$
85% (C ₂ F ₅) ₂ (SO ₂) ₂ NH	$6.7 \pm 1.0 \times 10^{-3}$	$3.62 \pm 1.0 \times 10^{-6}$

The polarization of the O₂ cathode (Fig. 5) has also been examined using high surface area Prototech gas-fed electrodes in 85% H₃PO₄ without and with 0.5% PFSL at 70 °C in a micro H₂/O₂ fuel cell (Fig. 6). The polarization is 70 mV less at a current density of 100 mA/cm² in the 0.5% PFSL solution. The polarization curves in the 0.5% PFSL + 85% H₃PO₄ solutions are independent of time over the 48 h time period of the experiments. This suggests that in the mixed electrolyte the concentration of PFSL is lower than the critical value which would promote flooding of the gas-fed electrodes. At lower concentrations (e.g., 0.126%) the PFSL still depresses the polarization at 70 °C but not by as much (≈ 30 mV at 100 mA/cm²).

The volatility of the PFSL in 85% H₃PO₄ at 150 °C was checked by heating the mixture in a beaker. After 5 h with a 4% PFSL + 85% H₃PO₄, a substantial amount of the PFSL was lost by evaporation. Thus the intrinsic vapor pressure of the PFSL itself is

too high for operations under acid fuel cell conditions (190 °C). A condenser system could be used to recover the PFSl from the vapor phase.

Other electrolytes which have been investigated in the authors' laboratory at both low and high concentrations with Prototech high area Pt electrodes are listed in Table II for either 70 or 100 °C together with polarization data. The relatively poor performance of the 84% (F₂SO₂)₂NH may be due to stability problems and/or impurities. The perfluorosulfonic carboxylic acid probably forms a self-assembled layer with the C₄F₉ tail closest to the interface.

IV. O₂ REDUCTION IN CONCENTRATED PERFLUORO BIS PHOSPHORIC ACID

The decrease in polarization for the Prototech Pt catalyzed O₂ cathode in 85% (HIO)₂OP-CF₂-CF₂-PO(OH)₂ as compared with 85% H₃PO₄ is quite substantial at 100 °C (see Table II). These electrodes have been operated in this electrolyte at 200 °C with relatively little increase in polarization over 500 h. The bis phosphoric acids were synthesized by Prof. D. Burton and his research group.¹³

V. THE ROLE OF O₂ SOLUBILITY

One of the important differences between the perfluoro-acids and H₃PO₄ is the much greater solubility of O₂. Higher solubility of O₂, however, does not necessarily mean lower polarization and faster kinetics.

To illustrate this, consider a reaction mechanism involving the following initial step as rate controlling.



With reaction (c) rate determining, the rate of the forward process can be given by¹⁵:

$$v_f = \frac{k_f}{\gamma_*} \cdot a_{\text{O}_2} \cdot a_{\text{Pt}} \quad (3)$$

where k_f is the forward rate constant, γ_* is the activity coefficient for the transition state, a_{O_2} is the activity of O₂ in the electrolyte phase and a_{Pt} is the activity of bare Pt sites. The interaction of water with the Pt sites is assumed to be weak.

The activity of O₂ in the electrolyte phase is controlled by the condition that the chemical potential of the dissolved O₂ be equal to that of the O₂ in the gas phase in equilibrium with the electrolyte phase; i.e.

$$(\mu_{\text{O}_2})_g = (\mu_{\text{O}_2})_e + RT \ln(a_{\text{O}_2})_e = (\mu_{\text{O}_2})_e + RT \ln(a_{\text{O}_2})_g \quad (4)$$

where the μ terms correspond to the chemical potentials of the subscripted species, the a terms are the activities and the μ^0 terms correspond to the standard state values. Thus the chemical potential of the O₂ in the electrolyte phase is independent of the

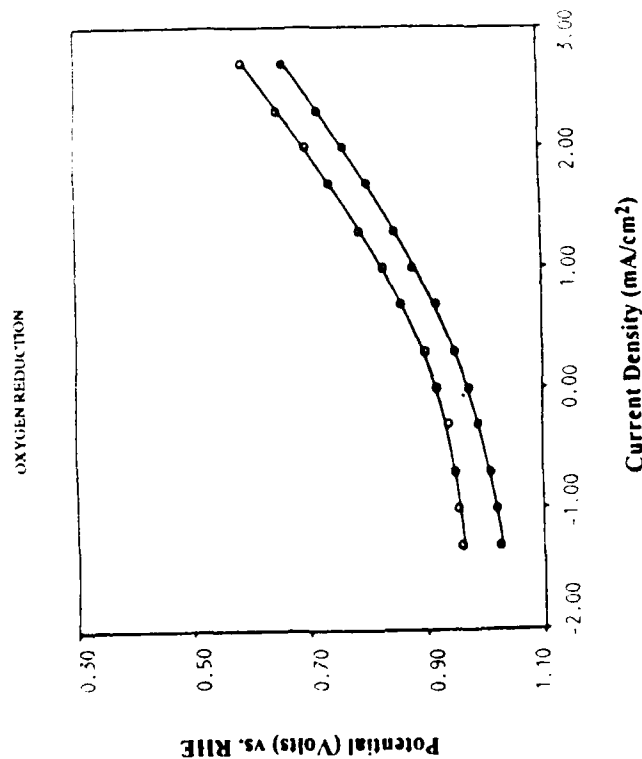


Fig. 5. Polarization curves for O₂ reduction on high-surface-area Prototech standard gas-fed electrode in 85% H₃PO₄ (O) and 85% H₃PO₄ containing 0.5% PFSl (●) at 70 °C.⁷

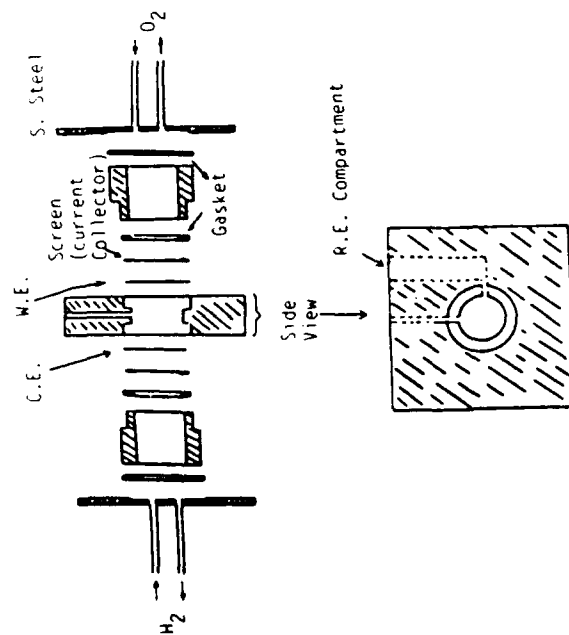


Fig. 6. Schematic representation of the micro-H₂ and O₂ fuel cell used to obtain polarization curves for gas fed high area Pt cathodes.

particular electrolyte phase provided the O_2 in the electrolyte phase is in equilibrium with the O_2 in the gas phase. The O_2 solubility should not directly influence the kinetics unless the reaction is under O_2 transport control in the gas and/or electrolyte phases. This can be seen by recalling from absolute rate theory¹⁶ that the rate constant k_1 in Eq. (3) is given by

$$k_1 = \frac{\kappa kT}{h} K_* = \frac{\kappa kT}{h} \cdot \exp - \frac{(\mu_*^\circ) - (\mu_{O_2}^\circ)_{el}}{RT} - (\mu_{Pt}^\circ) \quad (5)$$

where κ is the transmission factor, K_* is the apparent equilibrium constant for the $(O-O)_{ads}$ reactant in the transition state $(*)$, μ_*° is the chemical potential of the adsorbed oxygen in the transition state and the remaining symbols have their usual meaning. Recall that the equilibrium constant and chemical potential for the transition state are calculated from the partition functions with the vibration mode corresponding to transmission over the potential energy barrier omitted since it has already been used to derive the pre-exponential term $\kappa kT/h$. Combining Eqs. (3) and (5) yields

$$v_1 = \frac{\kappa kT}{\gamma_* h} \cdot \exp - \frac{(\mu_*^\circ) - (\mu_{O_2}^\circ)_{el}}{RT} - (\mu_{Pt}^\circ) \cdot (a_{O_2})_{el} (a_{Pt}) \quad (6)$$

and

$$v_1 = \frac{\kappa kT}{\gamma_* h} \cdot \exp - \frac{(\mu_*^\circ)}{RT} \cdot \exp \frac{(\mu_{O_2})_g}{RT} \cdot \exp \frac{(\mu_{Pt})}{RT} \quad (7)$$

with $(\mu_{O_2})_g = (\mu_{O_2})_{el} = \text{constant}$. The dependence of the kinetics on the factor $(a_{O_2})_{el}$ is offset by then term $\exp (\mu_{O_2}^\circ)_{el}/RT$ since $(\mu_{O_2})_g$ is held constant. The solubility of O_2 in the particular electrolytic solution has no direct effect on any term in Eq. (5a) but in a sense it may have a small indirect effect on the standard state chemical potential (μ_*°) of the $O-O$ species involved in the transition state. The interaction with the electrolytic solution in the transition state may have some similarity with the interaction of dissolved O_2 with the electrolytic solution. This effect would be expected to be quite small compared with that involving the change on the activity of the "bare" Pt (μ_{Pt}) in Eq. (7), particularly when specific adsorption of the electrolyte occurs on Pt. In general O_2 solubility has a substantial effect on the polarization curve for O_2 electroreduction only when mass transport of O_2 is controlling. Thus, it is not surprising that the solubility of O_2 drops off by a factor of 10^{-2} between 0.1 and 10 M KOH without a corresponding drop-off in the rate of O_2 reduction on Pt electrodes in concentrated KOH. Of course, for a given electrolyte-solvent system, the rate of adsorption of O_2 (e.g., reaction c) is proportional to the O_2 concentration with $(\mu_{O_2})_{el}$ constant (see Eq. (5)).

VI. ACIDITY

The strong electrolytes such as the sulfonic acids and the sulfonimides are many orders of magnitude stronger Brönsted acids than concentrated H_3PO_4 . If the rate determining step for O_2 reduction on Pt were first order in the H^+ activity, much larger differences in the rates of O_2 reduction would be expected than are observed. Further evidence that the rate determining step does not involve proton transfer includes the following:

- hydrogen-deuterium isotope studies of O_2 reduction on Pt in 85% H_3PO_4 and D_3PO_4 do not indicate any kinetic isotope effect¹⁰
- the rates of O_2 reduction on Pt in concentrated non-adsorbing acid solutions (e.g., $HClO_4$) and concentrated alkaline solutions (e.g., KOH) are within one order of magnitude of each other although the hydrogen ion activities differ by a factor of 10^{16} .

On the other hand, Šepa, Vojnović and Damjanović¹² have reported a value of $(\partial E_{SHE}/\partial pH)_1 = -0.12$ V for the potential range 0.85 to 0.70 V vs. SHE for O_2 reduction on Pt in 0.1 M H_2SO_4 . The bisulfate anion, however, is strongly adsorbed on Pt and this can complicate the evaluation of the pH dependence of the kinetics in H_2SO_4 solutions. In 0.1 M KOH, these authors report $(\partial E_{SHE}/\partial pH)_1 = 0$.

VII. ANOMALOUS TEMPERATURE POTENTIAL DEPENDENCE OF THE KINETICS

The observation of a substantial temperature dependence for α is not unique to the O_2 reduction reaction and includes hydrogen overpotential on various metals, even Hg.⁹ Various factors which may contribute to a temperature dependent apparent transfer coefficient have been discussed by Conway.⁹ Just why the effect is so large for O_2 reduction in acid electrolytes remains to be explained. One possibility is that the rate determining step does not involve a charge transfer process but rather the adsorption of a neutral species such as O_2 itself. Under such circumstances the potential dependence may be associated principally with an entropy of activation and its dependence on the potential gradient across the interface. This can result in an apparent value of α which is proportional to the absolute temperature.⁹

Scharifker *et al.*¹¹ also have examined the reduction of O_2 on Pt in concentrated H_3PO_4 at high temperatures and have concluded that the Tafel slope is proportional to the absolute temperature for O_2 reduction in concentrated H_3PO_4 . They propose that impurity effects cause the apparent temperature dependence of the transfer coefficient. The measurements of Scharifker *et al.* were made with microelectrodes and are subject to various problems such as leakage current. The studies in our laboratory have used the rotating disk technique.

Impurity effects can yield erroneous Tafel slopes but it is very unlikely that the Tafel slope would be -0.120 V/decade or $-2RT/F$ over a temperature range of 25 to 250 °C. The value at 25 °C reported by most researchers is -0.12 V/decade at 25 °C and not the value of -0.09 V/decade obtained by Scharifker *et al.* Further work is required to resolve this question.

VIII. COMPETITION OF O₂ WITH ELECTROLYTE COMPONENTS FOR ADSORPTION SITES

While water is important to the O₂ reduction reaction, the adsorption of H₂O or other polar species in the electrolytic solution may lead to a reduction in the accessibility of O₂ to the transition metal sites of the catalyst and hence a depression of the kinetics. There is little doubt that the adsorption of such species as HSO₄⁻, Cl⁻, and H₂PO₄⁻ depresses the kinetics of O₂ reduction on platinum.

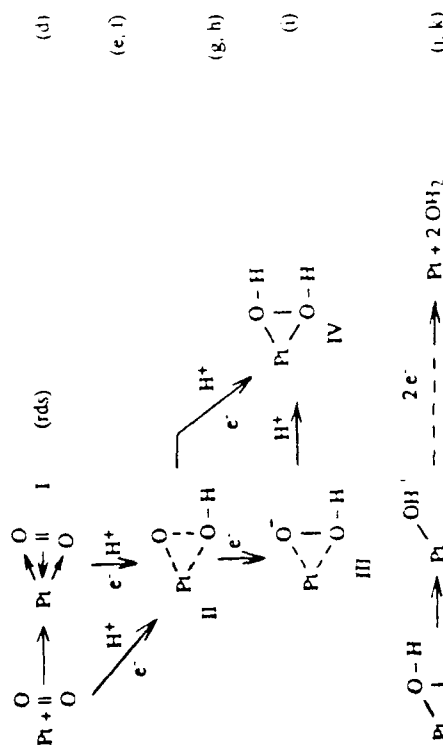
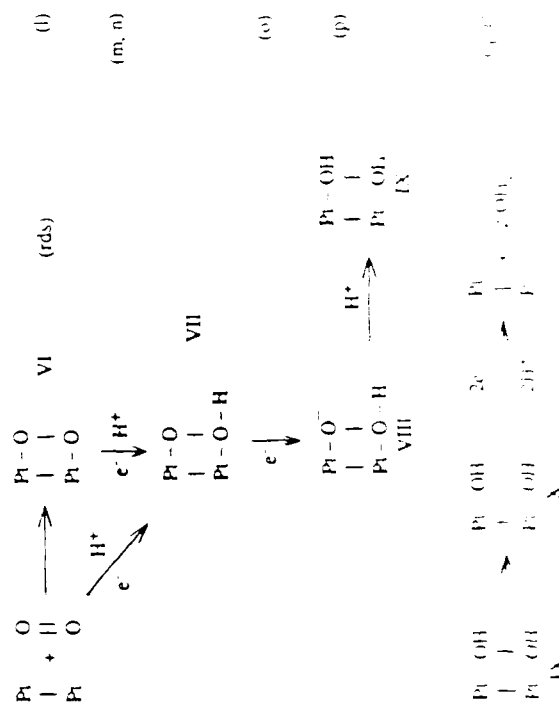
On the other hand, the formation of physically adsorbed layer of a surfactant type molecule such as C₄F₉-SO₂-NH-SO₂-CF₃ on the platinum surface promotes the O₂ reduction kinetics (see Section IV). This may be explained on the basis that the adsorbed perfluoro imide renders the interfacial region less polar and hence, favors O₂ adsorption in competition with polar components of the electrolyte for adsorption sites on the Pt. It may not be so much that the surfactant reduces the free energy of adsorption of the O₂ but rather it increases the free energy of adsorption of H₂O and ionic components because of the lower effective dielectric constant in the electrolyte phase immediately adjacent to the catalyst surface.

CONCLUSIONS CONCERNING THE ROLE OF THE ELECTROLYTE IN O₂ REDUCTION

The following are some of the conclusions reached by the authors concerning its role of the electrolyte in the kinetics of O₂ reduction in concentrated acid solutions.

1. Proton transfer is not involved in the rate determining step and is not an important factor in O₂ reduction kinetics in concentrated H₃PO₄.
2. The O₂ competes with various species in the electrolyte for adsorption sites on platinum catalyst and this in turn results in the depression of the kinetics. Anionic species such as Cl⁻, H₂PO₄⁻, HSO₄⁻ are particularly detrimental. In seeking new acid electrolytes, species which strongly adsorb on Pt and similar catalysts should be avoided.
3. Additives which form self assembled ordered films on Pt may lower the O₂ reduction overpotential significantly. The decrease may be explained on the basis of a decrease in the dielectric constant in the interfacial region caused by the additive. This increases the adsorption of O₂ as a non-polar species and decreases the adsorption of polar species such as the various phosphate species and even water itself.
4. Thermodynamic and kinetic considerations indicate that the O₂ solubility in the electrolytic solution should not have a direct effect on the rate of O₂ reduction at a fixed potential and fixed O₂ partial pressure in equilibrium with the electrolytic solution provided mass transport of O₂ in the electrolyte phase is not controlling.

Two mechanisms which meet this criteria are the following:

Mechanism I for O₂ ReductionMechanism II for O₂ Reduction (dual site)

In each case the rate determining step is the adsorption of O_2 on the Pt surface and the reaction is first order in O_2 concentration for a given electrolyte, as has been observed in rotating disk electrode studies. The differences between mechanism I and II is that mechanism I involves a single Pt surface atom while mechanism II involves two adjacent sites on two different Pt surface atoms.

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ИЗВОД

РЕДУКЦИЈА КИСЛОНИКА У РАЗЛИЧИТИМ КИСЕЛИМ ЕЛЕКТРОЛИТИМА

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Проучавања је електрохемијска редукција киселика у неколико нових киселих електролита и смеси ових електролита са концентрованим фосфорном киселином (којасе сада користи у H_2/O_2 горивним елементима). Одређене су поларизационе криве на платину са ротирајућом диском и диск-претензија грамама и наплатиније грамама са фосфорном киселином. Поларизационе криве показују да је механизам редукције киселика у овим електролитима различит од механизма редукције киселика у фосфорној киселини. Разматрања су могућности објашњења овог ефекта.

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